PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Improvements in or relating to the manufacture of Halogenated Hydrocarbons

We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, of Imperial Chemical House, Millbank, London, S.W.1, a British Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the manufacture of halogenated hydrocarbons.

In the specification of copending British Application No. 23106/62 (now Serial No. 968,933) a process is described for the manufacture of organic halides, for example, vinyl chloride which comprises contacting a gaseous mixture comprising an olefine, a hydrogen halide and a source of elemental oxygen, the concentration of oxygen being maintained below 10% by volume of the total feed, with a supported catalyst at elevated temperature, the catalyst comprising a compound of a metal of the platinum group, that is, a compound of one of the metals, platinum, palladium, rhodium, ruthenium, osmium and iridium.

We have now found that in such a process the activity of the catalyst is increased by incorporating with a compound of a platinum group metal a compound of a rare earth metal. By the increased activity of the present catalysts is meant that a specified amount of the catalyst of the present invention will give a greater amount of halogenated hydrocarbons than is obtained under similar reaction conditions when using the same amount of catalyst containing platinum but not containing a compound of a rare earth metal. Alternatively, a lesser amount of the catalyst of the present invention than that of the catalyst not containing a compound of a rare earth metal will give under similar reaction conditions similar amounts of halogenated hydrocarbons.

According to the present invention, therefore, we claim a process for the manufacture of halogenated hydrocarbons which comprises reacting an olefine with a hydrogen halide and a source of elemental oxygen, the concentration of oxygen being kept below 10% by volume of the total feed, at elevated temperature in the presence of a supported catalyst comprising a compound of a platinum-group metal as hereinafter defined and a compound of a rare earth metal.

By the term "a compound of a platinum-group metal" is meant a compound of one of the metals platinum, palladium, rhodium, ruthenium and iridium. Of these the preferred compound is a compound of platinum or rhodium. Compounds of any of the rare earth metals, that is, those elements of atomic numbers 57 to 71, may be used in the invention. Good results are obtained with a compound of cerium, lanthanum or neodymium.

Preferably the compound of the platinum-group metal and of the rare earth metal is a halide corresponding to the halogen of the halogenated compound produced. Another compound of a metal of variable valency may also be incorporated in the catalyst, preferably a halide corresponding to the halogen of the halogenated hydrocarbon produced. Thus in the production of vinyl chloride the catalyst suitably also contains copper chloride. The incorporation of alternative compounds to those of said metals of variable valency in a catalyst comprising a compound of a platinum group metal and a compound of a rare earth metal, for example, compounds, preferably the halides, of the alkali metals of group I of the Periodic Table is also beneficial. The preferred alkali metal is potassium.

The supported catalyst may be diluted with further quantities of untreated support or may be diluted with other materials such as graphite which assist in controlling the heat of the reaction. Again a graded bed may be used,

that is, a bed in which the ratio of untreated support or graphite particles to supported catalyst is greatest at the inlet end of the bed and is diminished from the inlet end to the outlet end of the bed.

The present process is particularly applicable to the manufacture of chlorinated and brominated hydrocarbons. Olefine reactants which may be employed include, for example, ethylene, propylene, straight and branched-chain olefines containing four or more carbon atoms, cyclic olefines such as cyclohexane, and olefines containing aryl groups such as styrene.

In the present process halogenated products other than the monohalogenated olefine are produced. For example, when using ethylene and hydrogen chloride as reactants, chlorinated hydrocarbons, such as 1:2-dichloroethane are produced as well as vinyl chloride.

Temperatures in the range 250° C. to 550° C. are generally employed although the particular temperature range employed depends on the particular olefine reactant employed. For example in the manufacture of vinyl chloride from ethylene temperatures in the range 250° C. to 500° C. preferably 300° C. to 450° C. are employed.

In order to prevent the reaction occurring with explosive violence the concentration of elemental oxygen is kept below 10%, for example 6% by volume. A gaseous diluent may be present, for example, nitrogen: thus a suitable source of elemental oxygen is air. The reaction may be carried out using excess with respect to oxygen of olefine such as ethylene and/or of excess hydrogen halide such as hydrogen chloride. Preferably an excess over the stoichiometric amount of olefine with respect to oxygen is employed and the unreacted olefine is recycled. Preferably also the process is operated with an excess of olefine such as ethylene, with respect to oxygen, such that, based on a single pass, a conversion of ethylene to all products (that is, chlorinated products as well as CO and CO_2) of less than 80% is achieved. By this means an enhanced amount of monochloro-substituted product is obtained. The reactants and diluent may be premixed before passing to the reaction zone or may be passed directly into the reaction chamber wherein mixing and reaction takes place.

The following Examples illustrate but do not limit the invention.

EXAMPLE 1

A catalyst was prepared by dissolving 16.9 g. $CuCl_2.2H_2O$ and 6.6 g. $CeCl_3$ in 23 ml. water. To this solution was added a solution of 3.1 g. chloroplatinic acid (containing 40% Pt by wt.) in 15 ml. water. The combined solution was added to 100 g. of an activated alumina known under the trade name 'Actal' A (Registered Trade Mark) which was placed in an evaporating dish and the mixture was stirred with a glass rod. The impregnated alumina was then dried by heating for 18 hours at 120° C. The supported catalyst thus contained 5% by wt. Cu, 1% by wt. Pt, and 3% by wt. Ce. The supported catalyst was of particle size which passed through a 10 mesh sieve and was retained by an 18 mesh sieve. The aperture between the wires for a 10 mesh sieve is 1.68 mm. and for an 18 mesh sieve is 0.85 mm.

Utilising a catalyst tester unit 1 ml. of the catalyst was diluted with 30 ml. of glass particles of the same size as the alumina. The mixtures was placed in a 'Pyrex' tube ('Pyrex' is a Registered Trade Mark) $\frac{3}{4}$ inch internal diameter, equipped with a central thermocouple pocket $\frac{1}{4}$ inch external diameter. The reactor was maintained at a temperature of about 350° C. and a gas mixture consisting of 2.5 l./hr. ethylene, 5 l./hr. anhydrous HCl, 1 l./hr. oxygen and 8.5 l./hr. nitrogen was passed over the heated catalyst. After about an hour when static conditions had been established, the exit stream was analysed and found to contain:

	% by volume
$CH_2=CHCl$	3.0
$CH_2Cl.CH_2Cl$	3.5
CO	0.1
CO_2	0.7
O_2	1.5
HCl	19.5
C_2H_4	7.8
N_2	56.6
H_2O	7.3

In a similar procedure similar results to those given above were obtained when using a catalyst containing 0.25% by wt. Pt, 5% by wt. Cu and 3% by wt. Ce.

EXAMPLE 2

16.9 g. $CuCl_2 2H_2O$ and 6.6 g. $CeCl_3$ were dissolved in 65 ml. water. To this solution was added 3.1 g. of a chloroplatinic acid (containing 40% Pt by wt.) dissolved in 15 ml. water. The combined solution was added to 100 g. silica gel, particle size 10—18 mesh contained in an evaporating dish and the mixture was stirred with a glass rod. The impregnated silica gel was dried by heating for 18 hours at 120° C. The catalyst contained 5% by wt. Cu, 3% by wt. Ce and 1% by wt. Pt.

In this Example and Examples 3 to 5 and 9 to 12 the supported catalyst was diluted with graphite of the same particle size. This catalyst bed was in 4 sections of equal volume. The 1st, 2nd and 3rd sections were diluted with decreasing amounts of graphite such that

they contained 10%, 30% and 70% of the supported catalyst. The 4th section of the catalyst contained no graphite. The catalyst was placed in a 'Pyrex' tube ('Pyrex' is a Registered Trade Mark) ¾ inch internal diameter, equipped with a central thermocouple pocket, ¼ inch external diameter. The tube was heated externally by electrical wiring. The temperature of the furnace was 330° C. and the temperature of the hot spot was 370° C. to 390° C. The feed mixture passed through the heated catalyst was 5 l./hr. ethylene 10 l./hr. anhydrous HCl, 2 l./hr oxygen and 17 l./hr. nitrogen.

After about an hour when static conditions had been established, the analysis of the gas stream was found to be as follows:—

	% by volume
$CH_2=CHCl$	2.7
$CH_2Cl.CH_2Cl$	8.5
CO	0.03
CO_2	0.2
O_2	0.7
HCl	13.3
C_2H_4	5.1
Na_2	58.2
H_2O	11.3

Example 3

The procedure of Example 2 was repeated except that 1% palladium instead of 1% platinum was incorporated in the catalyst. (In the preparation of the catalyst 2.1 g. $PdCl_2$ in 10 ml. of water and 10 ml. concentrated HCl were added to the cupric chloride solution).

After about 1 hour when static conditions had been established the analysis of the gas stream was found to be as follows:—

	% by volume
$CH_2=CHCl$	0.9
$CH_2Cl.CH_2Cl$	2.5
CO	0.2
CO_2	0.4
O_2	0.4
HCl	26.8
C_2H_4	9.1
N_2	55.5
H_2O	4.2

Example 4

This Example was carried out to illustrate that the amount of vinyl chloride is increased by using an excess of ethylene above the stoichiometric amount with respect to oxygen.

The catalyst employed was of the composition disclosed in Example 2. Feed of 2 to 10 l./hr. ethylene, 10 l./hr. anhydrous hydrogen chloride and either 1 or 2 l./hr. oxygen were passed over the catalyst. The total gas feed was regulated to 34 l./hr. by addition of the requisite amount of nitrogen.

In Runs 1 (a) and 1 (d) the molar ratio of C_2H_4 to O_2 was 2:1 and this represents the stoichiometric amount required for the reaction of C_2H_4, O_2 and HCl to give vinyl chloride.

The results are indicated in Table I.

TABLE I

Run	O_2 fed (l./hr.)	C_2H_4 fed (l./hr.)	C_2H_4 conversion to all products	$CH_2=CHCl$ produced (l./hr.)
1 (a)	1	2	100	0.1
1 (b)		3	70	0.4
1 (c)		5	42	0.6
1 (d)	2	4	93	0.6
1 (e)		5	68	0.7
1 (f)		10	34	1.0

Example 5

The Example was carried out utilising the procedure of Example 1 except that the support was a diatomaceous earth, known under the Trade Mark 'Celite'.

After about 1 hour when static conditions had been established the analysis of the product was found to be as

	% by volume
$CH_2=CHCl$	2.4
$CH_2Cl.CH_2Cl$	4.7
CO	0
CO_2	0.2
O_2	2.3
HCl	21.2
C_2H_4	8.0
N_2	53.6
H_2O	7.6

Example 6

A catalyst was prepared by dissolving 23.5 g. $CeCl_3$ and 10.2 g. KCl in 58 ml. water. The solution was added to 100 g. of an activated alumina known under the Trade Mark 'Actal' A (Registered Trade Mark) which was placed in an evaporating dish and the mixture was stirred with a glass rod. The impregnated alumina was then dried by heating for 5 hours at 120° C. This was then reimpregnated with a second solution consisting of 1.1 g. of ammonium chlororhodite (containing 30% rhodium) dissolved in hydrochloric acid. The alumina was then dried again for 5 hours at 120° C. The supported catalyst contained 10% by wt. cerium, 4% by wt. potassium and 0.25% by wt. rhodium. The particle size of the catalyst was the same as that of Example 1.

40 ml. of undiluted catalyst was placed in the apparatus described in Example 1. The reaction was maintained at a temperature of 400° C. and a gas mixture consisting of 15.2 l./hr. N_2, 8.7 l./hr. HCl, 4.4 l./hr. C_2H_4 and 1.8 l./hr. O_2 was passed over the heated catalyst. When steady conditions had been reached the exit stream was analysed and found to contain

	% by volume
$CH_2=CHCl$	3.6
$CH_2Cl.CH_2Cl$	0.3
$CH_3.CH_2Cl$	0.02
CO	0.06
CO_2	1.92
O_2	1.1
HCl	24.7
C_2H_4	9.3
N_2	53.1
H_2O	5.9

Example 7

This Example was carried out utilising the procedure of Example 1 except that the catalyst contained 5% Cu, 3% La and 1% Pt.

When steady conditions had been established the exit stream was analysed and found to contain:

	% by volume
$CH_2=CHCl$	3.0
$CH_2Cl.CH_2Cl$	3.8
CO	0.2
CO_2	0.55
O_2	1.5
HCl	18.9
C_2H_4	7.55
N_2	56.9
H_2O	7.6

Example 8

This Example was carried out utilising the procedure of Example 1 except that the catalyst contained 5% Cu, 3% Nd and 1% Pt.

When steady conditions had been established the exit stream was analysed and found to contain:

	% by volume
$CH_2=CHCl$	2.6
$CH_2Cl.CH_2Cl$	3.4
CO	0.1
CO_2	0.5
O_2	2.0
HCl	20.1
C_2H_4	8.4
N_2	56.3
H_2O	6.6

Example 9

This Example was carried out using the same catalyst and conditions of Example 2 except that the organic feed consisted of 5 l./hr. propylene.

After about 1 hour when static conditions had been established the exit stream was analysed and found to contain:

	% by volume
1:2-dichloropropane	0.5
2-chloropropane	2.2
Chloropropenes	4.3
CO	0.1
CO_2	0.2
O_2	3.4
HCl	23.2
C_3H_6	8.3
N_2	52.6
H_2O	5.2

Example 10

This procedure was carried out as in Example 9 except that a catalyst was employed containing 1% by weight Pd instead of 1% Pt (containing Cu and Ce and prepared in the manner described in Example 2).

After about 1 hour when static conditions had been established the analysis of the gas stream was found to be as follows.

	% by volume
1:2-dichloropropane	1.7
2-chloropropane	1.7
Chloropropenes	2.5
CO	0.4
CO_2	0.6
O_2	2.7
HCl	23.3
C_3H_6	9.3
N_2	52.6
H_2O	5.2

EXAMPLE 11

The procedure of Example 9 was repeated except that the feed consisted of 5 l./hr. of isobutene.

After about 1 hour when static conditions had been established the analysis of the gas stream was found to be as follows:

	% by volume
1- and 3-chloro-2-methyl propenes	2.5
Tertiary butyl chloride	4.0
CO	0.3
CO_2	1.2
O_2	2.8
HCl	24.3
C_4H_8	8.6
N_2	52.3
H_2O	4.0

EXAMPLE 12

The procedure of Example 11 was repeated except that a catalyst was employed containing 1% by wt. Pd (containing Cu and Ce and prepared in the manner described in Example 2).

After about 1 hour when static conditions had been established the analysis of the gas stream was found to be as follows.

	% by volume
1- and 3-chloro-2-methyl propenes	1.5
Tertiary butyl chloride	3.3
CO	0.3
CO_2	1.8
O_2	3.0
HCl	5.4
C_4H_8	9.7
N_2	51.4
H_2O	3.6

WHAT WE CLAIM IS:—

1. A process for the manufacture of halogenated hydrocarbons which comprises reacting an olefine with hydrogen halide and a source of elemental oxygen, the concentration of oxygen being kept below 10% by volume of the total feed gases, at elevated temperature in the presence of a supported catalyst comprising a compound of a platinum group metal as hereinbefore defined and a compound of a rare earth metal.

2. A process as claimed in Claim 1 in which the compound of the platinum group metal is a compound of platinum.

3. A process as claimed in Claim 1 in which the compound of the platinum group metal is a compound of rhodium.

4. A process as claimed in any of the preceding claims in which the compound of a rare earth metal is a compound of cerium, lanthanum or neodymium.

5. A process as claimed in any of the preceding claims in which another compound of a metal of variable valency is incorporated in the catalyst.

6. A process as claimed in Claim 5 in which said metal of variable valency is copper.

7. A process as claimed in Claims 1 to 4 in which a compound of an alkali metal, of group I of the Periodic Table, preferably potassium, is incorporated in the catalyst.

8. A process as claimed in any of the preceding claims in which the catalytic compounds employed are halides corresponding to the halogen of the halogenated hydrocarbons produced.

9. A process as claimed in any of the preceding claims in which the catalyst is diluted with further quantities of a support material or is diluted with other materials such as graphite which assist in controlling the heat of the reaction.

10. A process as claimed in Claim 9 wherein a graded bed of catalyst is employed.

11. A process as claimed in any of the preceding claims in which a reaction temperature in the range 250° C. to 550° C. is employed.

12. A process as claimed in any of the preceding Claims 1 to 11 in which the olefine is propylene.

13. A process as claimed in any of the preceding Claims 1 to 11 in which the olefin is a straight or branched-chain olefin containing 4 or more carbon atoms.

14. A process as claimed in any of the preceding Claims 1 to 11 in which the olefine is a cyclic olefin.

15. A process as claimed in Claim 14 in which the cyclic olefine is cyclohexene.

16. A process as claimed in any of the preceding Claims 1 to 11 in which the olefine is one containing an aryl group.

17. A process as claimed in Claim 16 in which the olefine is styrene.

18. A process as claimed in any of the preceding Claims 1 to 17 in which the reaction is carried out in the presence of a gaseous diluent.

19. A process as claimed in Claim 18 in which the gaseous diluent is nitrogen.

20. A process as claimed in any of the preceding Claims 1 to 11, 18 and 19 in which

the olefine reactant is ethylene and in which a reaction temperature in the range of 250° C to 500° C. preferably 300° C. to 450° C. is employed.

21. A process as claimed in Claim 20 in which an excess of olefine reactant with respect to oxygen is employed and in which unreacted olefine is recycled.

22. A process as claimed in Claims 20 and 21 in which the process is operated with excess of ethylene with respect to oxygen such that, based on a single pass, a conversion of ethylene to all products (that is chlorinated products as well as CO and CO_2) of less than 80% is achieved.

23. A process for the manufacture of chlorinated hydrocarbons substantially as described with reference to the Examples.

24. Halogenated hydrocarbons whenever manufactured by a process as claimed in any of the preceding claims.

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